

Introduction of Karl Fischer Coulometric Titrator with Single-Chamber Electrolysis Method

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1. Introduction

Water-content analyzers based on the Karl Fischer (KF) coulometric titration method allow accurate measurement of trace water content (on the order of micrograms) by exploiting the following advantages:

1. The KF reaction is highly water-selective; this allows high-precision measurements of water alone if no side reactions occur.
2. Coulometric titration is an absolute determination technique in which the mass of a given substance is determined by measuring the quantity of electricity required to electrolyze that substance; it does not necessarily require a standard solution.
3. An electrolytic current of 1 mA flowing for 1 second—a current and time duration that are easily measured—yields a charge of 1 mC, corresponding to just 93.4 ng of water. Thus the technique allows high-sensitivity measurements.

For these reasons, KF coulometric titration is widely used in quality-control analysis for liquid, solid, and gaseous samples.

KF coulometric titration methods may be classified into two-chamber and single-chamber electrolysis methods, depending on the structure of the electrolysis cell. At present, single-chamber electrolysis methods are not among the official methods described by Japanese Pharmacopoeia and other sources, and for this reason two-chamber methods are the most commonly used. However, single-chamber methods offer a number of advantages, including the fact that they do not need a counter-electrode solution—thus reducing running costs—and that the simple structure of the electrolysis cell makes the apparatus easier to maintain. For these reasons, in the future we expect that single-chamber instruments will be adopted for use in a wide range of fields.

In this article, we will discuss water-content measurement via single-chamber electrolysis using a Hiranuma AQ-2200AF trace water-content analyzer (Figure 1).



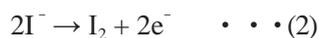
Fig. 1 Hiranuma AQ-2200AF trace water-content analyzer.

2. Principles of operation

In this section, we discuss the principles underlying KF coulometric titration measurements. These measurements are based on the following equation, known as the KF reaction:



In coulometric measurements, iodine is produced electrochemically through anode oxidation, as expressed by:



Water present in a sample is consumed by the KF reaction until a slight excess of iodine has accumulated; this is detected by twin platinum electrodes and defines the end of the titration. From the total quantity of electricity (charge) required to proceed the electrolysis process to the end of the titration, Faraday's law can be used to determine the mass of water consumed by the KF reaction.

Two-chamber electrolysis methods, which have long been used, employ a diaphragm to separate the anode and cathode of the electrolysis reaction; this prevents diffusion of substances that obstruct the KF reaction, such as reduction products at the electrolysis cathode. In single-chamber electrolysis methods, the anode and cathode are immersed in the same electrolytic solution, and thus—unless the electrolysis is controlled by methods discussed below—KF reaction products produced at the cathode diffuse throughout the electrolytic liquid, obstructing the progress of the KF reaction and resulting in significant fluctuations in measured results.

An effective method for limiting the generation of undesirable reaction product at the cathode in single-chamber electrolysis is to control the density of the electrolysis current at the cathode. The current density is determined by the total electrolysis current and the electrode surface area. If the current density lies below the optimal range for KF coulometric titration, undesirable reaction products are generated as reduction products, while if the current density is too large then it is not possible to increase the electrolysis current to its required value.

For single-chamber electrolysis method, the AQ-2200A is equipped with two separate cathodes with different surface areas, with one or the other electrode chosen as appropriate for the electrolysis current used. This is to limit the production of undesirable reaction products and to maintain the current density at the cathode in the appropriate range for both background measurements and sample measurements, even as the total electrolysis current varies widely—roughly over the range 0.1-300 mA—between the two types of measurements (Figure 2).

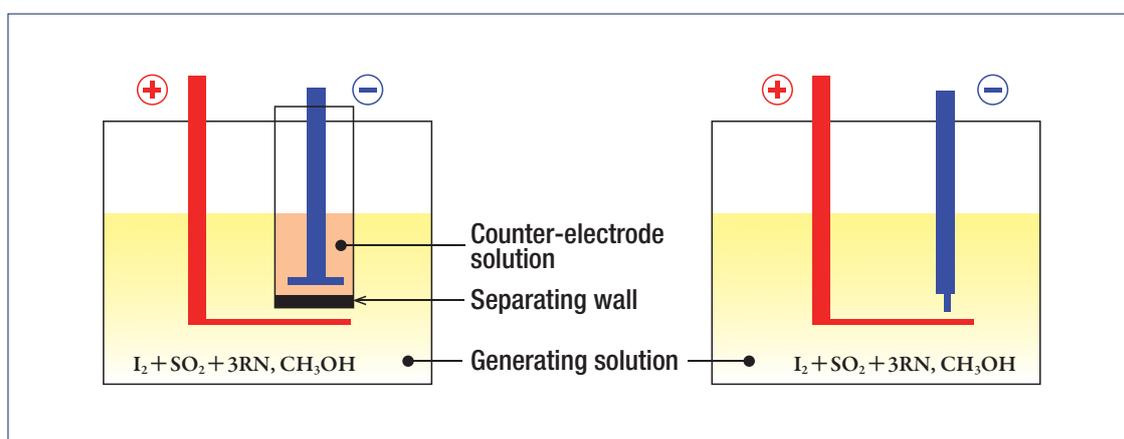


Fig. 2 Schematic diagram of electrolysis electrodes in two-chamber electrolysis method (left) and single-chamber electrolysis method (right).

3. Sample measurements

Table 1 shows the results of measurements of various samples using both two-chamber and single-chamber electrolysis methods, with each measurement repeated 3 times.

The conditions under which these measurements were made are as follows.

1. Instrument: Hiranuma AQ-2200AF trace water content analyzer
2. Measurement conditions and parameters: We use the initial conditions and vary only the electrolytic cell settings as appropriate.
3. Electrolytic cells: Standard (two-chamber) electrolytic cell, single-chamber electrolytic cell (Figure 3)
4. Generating solution: AQUALYTE RS-A
5. Counter-electrode solution: AQUALYTE CN (used only for the standard cell)

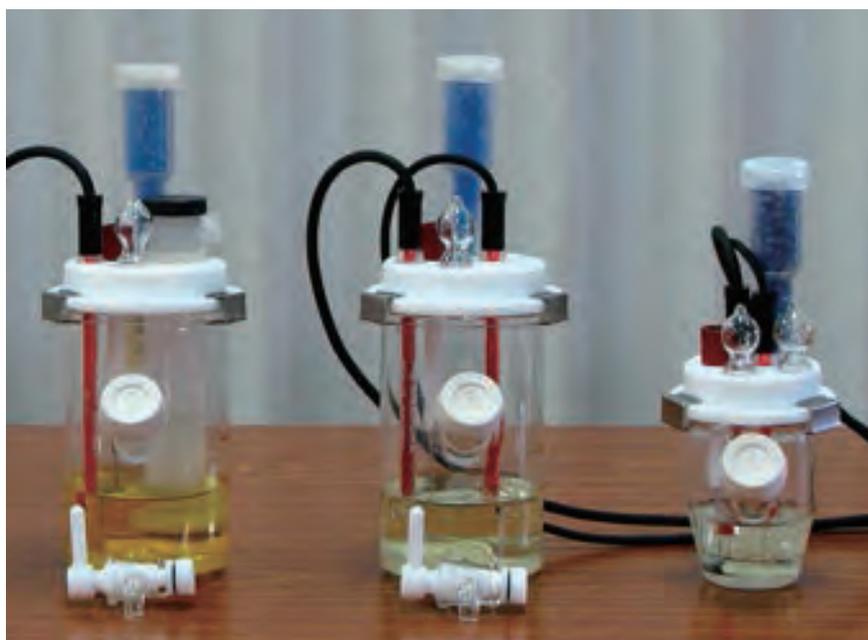


Fig. 3 Electrolytic cells. From left to right: Standard electrolytic cell, single-chamber electrolytic cell, low-capacity single-chamber electrolytic cell.

Table 1 Measurements of various samples using two-chamber and single-chamber electrolysis methods

Measurement method	Sample	Measured water content (two-chamber electrolysis cell)			Measured water content (single-chamber electrolysis cell)		
Direct method	Chloroform	30.7	± 0.7	ppm	30.2	± 0.8	ppm
	2-propanol	91.7	± 0.6	ppm	90.5	± 0.7	ppm
	Toluene	53.5	± 0.2	ppm	52.7	± 0.5	ppm
	Cyclohexane	38.0	± 0.7	ppm	37.4	± 0.2	ppm
	Anisole	163.9	± 0.1	ppm	163.3	± 0.5	ppm
	Acetonitrile	99.3	± 2.0	ppm	99.8	± 1.2	ppm
	Ethyl acetate	222.8	± 0.1	ppm	223.5	± 0.1	ppm
	Acetic acid	152.7	± 1.2	ppm	157.1	± 0.8	ppm
	m-Cresol	1432.4	± 1.8	ppm	1432.2	± 0.8	ppm
	Pyridine	589.3	± 1.3	ppm	594.2	± 0.9	ppm
Distillation	Biodiesel	618.8	± 4.0	ppm	617.0	± 0.9	ppm
	Kerosene	50.3	± 0.9	ppm	54.4	± 0.9	ppm
Evaporation	Sodium tartrate dihydrate	15.420	± 0.040	%	15.440	± 0.040	%
	Oil shale	0.690	± 0.007	%	0.693	± 0.014	%

4. Key advantages of the AQ-2200AF

In this section we note the key advantages of single-chamber electrolysis method using the AQ2200AF.

1. Almost any substance that can be measured via the two-chamber electrolysis method can be measured via the single-chamber electrolysis method. (Some exceptions exist; for example, precise measurements of nitro compounds are difficult due to production of water through cathode reduction.)
2. Many types of generating solution may be used.
Suitable liquids include AQUALYTE RS-A, GRO-A, RS, RO, and HYDRANAL[®] Coulomat AK (Hayashi Pure Chemical Industries, Ltd.)
3. Reduction in running costs
Single-chamber electrolysis cell:
 - Eliminates the need for a counter-electrode solution.Low-capacity single-chamber electrolysis cell:
 - Reduces amount of generating solution involving infrequent water-content measurements.
4. Ease of use
The internal structure of the single-chamber cell is simpler than that of a standard cell, thus streamlining cleaning and other maintenance operations.

5. Conclusions

In this article we introduced the AQ-2200AF, an instrument primarily optimized for measurements of sample water content at the ppm level with applications to a wide variety of samples, including chemical products, petroleum products, oil, paint, and pharmaceuticals. We are confident that customers using the AQ-2200AF will be fully satisfied with the many advantages this product offers.

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